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Infrared properties of the organic semiconductor MEM(TCNQ)₂ in its high-temperature phase

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The infrared spectrum of N-methyl-N-ethylmorpholinium tetra-cyanoquinodimethane, MEM(TCNQ)₂, at temperatures above the phase transition at $T = 335$ K is reported. The oscillator strength associated with charge-transfer processes is shifted down in frequency as compared to the room-temperature phase. The sharp vibrational structure observed at 300 K is considerably broadened. The derived linear electron-molecular-vibration coupling constants are almost unchanged from those obtained at 300 K, thus confirming the theoretical framework used.

I. INTRODUCTION

Recent investigations¹⁻⁴ of the physical properties of the complex TCNQ salt N-methyl-N-ethylmorpholinium-tetracyanoquinodimethane, MEM(TCNQ)₂, revealed three structural phases. In the region $T \leq 20$ K the planar TCNQ molecules in MEM(TCNQ)₂ form a tetramerized linear-chain structure.⁴ Between 20 and 335 K MEM(TCNQ)₂ exists in a triclinic phase [room-temperature (RT) phase] in which the linear TCNQ chains are strongly dimerized with alternating interplanar distances of 3.15 and 3.27 Å.² The optical properties in the dimerized phase were reported and discussed by Rice and the present authors.⁵ It was found that each unpaired electron is localized on a dimeric TCNQ unit and the data were used to deduce values for the intradimer hopping integral (t), the TCNQ α_g molecular-vibration frequencies (ω_α), and the linear electron-molecular-vibration (EMV) coupling constants (g_α).

At approximately $T = 335$ K MEM(TCNQ)₂ undergoes a transition to a third structural phase [high-temperature (HT) phase], in which the TCNQ molecules are stacked almost uniformly.⁴ The dc conductivity jumps discontinuously from 10^{-2} ($\Omega \text{ cm}$)⁻¹ to about 30 ($\Omega \text{ cm}$)⁻¹ and is only weakly temperature dependent above 335 K. This is indicative of a considerable delocalization of the b_{2g} π -molecular-orbital electrons of the TCNQ molecules.

The one-electron energy bands can be expected to change as sketched in Fig. 1. The half-filled lower band in the RT phase, Fig. 1(b), is narrow as a result of poor interdimer overlap, hence the dc-conductivity is low. The optical properties of this phase for photon energies $\hbar\omega \gg t'$ (t' is the interdimer overlap integral) are found to be close to those of an isolated dimeric unit.⁵ On the other hand, in the HT phase, the TCNQ molecules are only slightly dimerized, Fig. 1(c), and

the half-filled conduction band has a considerable width, therefore resulting in a fairly high, although not metallic dc conductivity.

In this addenda to Ref. 5 we report the optical spectrum in the HT phase. The data are analyzed in terms of the phase phonon theory by Rice,⁶ which is appropriate in a system with delocalized electronic states. The resulting coupling constants (g_α) as obtained in the two different phases using two different theoretical models are compared. We consider this to constitute an important check of the reliability of coupling constants deduced from infrared spectra.

II. EXPERIMENTAL RESULTS

Reflectance data at $T = 350$ K, polarized along the TCNQ stacks, was obtained in the frequency range 600–14 000 cm^{-1} by experimental procedures as described in Ref. 5. The data was analyzed by a Kramers-Kronig transformation to obtain the frequency-dependent conductivity. Extrapolation procedures were consistent with the known dc conductivity at low frequency and assumed the same high-frequency behavior as at 300 K.

The infrared part of the conductivity spectrum is shown in Fig. 2(a). With a dc conductivity of $\sim 20 \Omega^{-1} \text{ cm}^{-1}$ the optical spectrum is one of a semiconductor. Presumably the oscillator strength in the infrared is mainly associated with the band to band transition shown in Fig. 1(c). The change

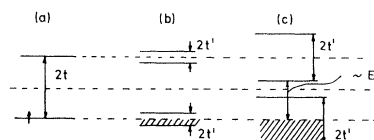


FIG. 1. Schematic energy band spectrum for (a) isolated TCNQ dimer, (b) chain of quasi-isolated TCNQ dimers ($t' \ll t$), and (c) chain of strongly interacting TCNQ dimers ($t' \leq t$).

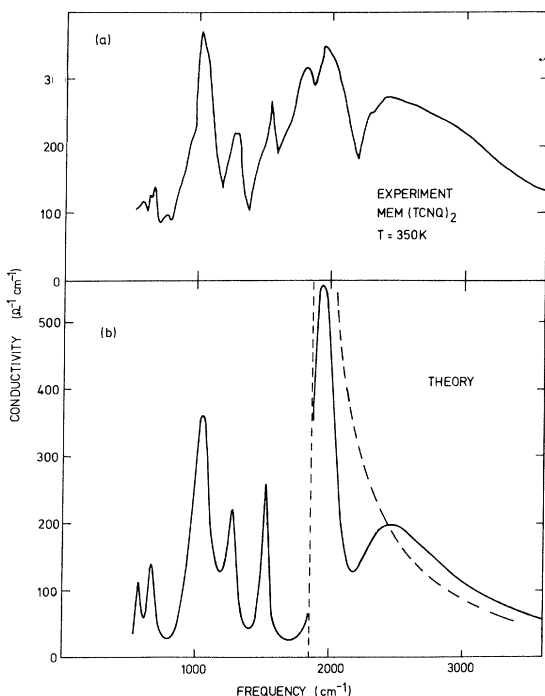


FIG. 2. Real part of the frequency-dependent conductivity along the crystallographic c axis of MEM(TCNQ)₂ at $T = 350$ K. Experimental data (a) and theoretical fit (b) are shown.

from the RT spectrum⁵ is rather drastic. The oscillator strength connected to charge transfer processes along the stacks has shifted down considerably. The very sharp molecular lines seen at 300 K are severely broadened and to some extent shifted in frequency.

III. ANALYSIS AND DISCUSSION

We analyze the data within the phase phonon theory by Rice.⁶ The frequency-dependent con-

ductivity is given by^{6,7}

$$\sigma(\omega) = \frac{\omega_p^2}{4\pi i \omega} \left[f\left(\frac{\omega}{2\Delta}\right) - f(0) - \left(\frac{\omega}{2\Delta}\right)^2 f^2\left(\frac{\omega}{2\Delta}\right) \lambda D_\phi(\omega) \right], \quad (1)$$

where ω_p denotes the plasma frequency of the non-interacting conduction electrons. 2Δ is the energy gap of the stabilized semiconducting state. The function

$$f(x) = \left(\pi i + \ln \left| \frac{1-S}{1+S} \right| \right) \frac{1}{2Sx^2}, \quad S = (1-x^2)^{1/2} \quad (2)$$

$$D_\phi(\omega)^{-1} = D_0(\omega)^{-1} + 1 - \frac{V}{\Delta} + \left(\frac{\lambda \omega^2}{4\Delta^2} \right) f\left(\frac{\omega}{2\Delta}\right), \quad (3)$$

and

$$D_0(\omega) = - \sum_n \frac{(\lambda_n/\lambda) \omega_n^2(q_0)}{\omega_n^2(q_0) - \omega^2 - i\omega\Gamma_n}. \quad (4)$$

The summation runs over all involved phonon bands. $2V$ is the energy gap in the absence of EMV coupling, $\lambda_n = N(0)g_n^2/\omega_n(g_0)$ is the dimensionless EMV coupling constant and $\lambda = \sum \lambda_n$. $N(0)$ denotes the density of states at the Fermi level (per molecule, both spin directions) of the original, noninteracting system of conduction electrons. g_n is the linear EMV coupling constant for the n th phonon, and ω_n and Γ_n the frequency and natural width of the n th phonon. Finally q_0 is the wave vector involved in the formation of the semiconducting state.

A fit of Eqs. (1)–(4) to the experimental $\text{Re}\sigma(\omega)$ spectrum is shown in Fig. 2(b). The indentation at 1860 cm^{-1} is interpreted as the semiconducting gap 2Δ . This value is consistent with the value of the intradimer overlap integral $t = 1580 \text{ cm}^{-1}$ deduced in the RT phase.⁵

The resulting TCNQ monomer molecular vibration frequencies ω_n and EMV coupling constants g_n are listed in Table I together with the g_n values

TABLE I. Electron-molecular-vibration coupling constants g_n .

Mode	ω_n (cm^{-1})	MEM(TCNQ) ₂ ^a ($T = 300$ K) (cm^{-1})	MEM(TCNQ) ₂ ($T = 350$ K) (cm^{-1})	Calculated ^b (cm^{-1})
1	3070	44	44 ^c	31
2	2210	350	400	423
3	1630	540	470	1057
4	1395	500	360	392
5	1180	300	300	229
6	958	85	85 ^c	237
7	718	190	210	263
8	597	50	100	18
9	324	180	180 ^c	194
10	150	75	75 ^c	78

^aAfter Ref. 5.

^bAfter Ref. 8.

^cCorresponding a_g modes do not explicitly show up in the reflectivity spectrum or are outside experimental range. RT phase values were used without disagreement with experiment.

obtained in the RT phase as well as previous theoretical estimates of the same in the isolated molecule. The ω_n are found to be unchanged from the RT phase within experimental accuracy. The new g_n values are reasonably consistent with the previous. No systematic change is found.

The discrepancies of experimental and theoretical values in the vicinity of the gap $\omega \sim 2$ may be anticipated since the theory⁶ was derived for $T = 0$, and qualitatively an energy redistribution of the conduction electrons should lead to the observed features.

The sum λ_{intra} of the deduced intramolecular EMV coupling constants λ_n is $\lambda_{\text{intra}} \sim 0.5$. As in Ref. 7 we have introduced in Eq. (1), a coupling $\lambda_{\parallel} = 0.1$ to a single low-frequency phonon $\omega_{\parallel}(q_0) = 64 \text{ cm}^{-1}$ to allow for coupling of the conduction electrons in MEM(TCNQ)₂ to low-frequency intermolecular phonons. Addition of λ_{intra} and λ_{\parallel} gives a total coupling parameter $\lambda = 0.6$, which together with the deduced parameters $V/\Delta \sim 0.25$ and $\omega_p = 4500 \text{ cm}^{-1}$ may be used to estimate the static dielectric constant as derived from Eq. (1):

$$\epsilon_s = 1 + \left(\frac{\omega_p}{2\Delta} \right)^2 \left| \frac{2}{3} + \lambda \frac{\Delta}{V} \right| = 18. \quad (5)$$

The smallness of V/Δ indicates a small value of the unrenormalized gap, $2V$, and is consistent with a slight dimerization in the HT phase of MEM(TCNQ)₂ arising from the neighboring MEM donor chains.⁴

IV. CONCLUSION

The main result of the present paper is the invariance of derived molecular parameters with respect to different models and different phases of the same material. This finding gives additional confidence in the theoretical basis^{5,6,9} for deducing these parameters and in the use of the models for the different electronic states.

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